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ScienceDirect

Physics Procedia 50 (2013) 405 – 409

Physics Procedia

International Federation for Heat Treatment and Surface Engineering 20th Congress
Beijing,China,23-25 October 2012

# Research on the mechanical and thermal properties of MWCNTs/CF reinforced epoxy resin matrix composite patch

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**Abstract**

The mechanical and thermal properties of multi-walled carbon nano-tubes and carbon fiber reinforced epoxy resin matrix composite patch were tested, which was prepared by the hand lay-up method. The results indicated that the imagination observed by SEM presented good resin-impregnation for both of the two kinds of composite patches, and the mechanical and thermal properties of composite patch could be effectively increased by improvement of the interface combination after adding MWCNTs. For the mechanical properties of composite patch reinforced with MWCNTs, the interlaminar shear strength, bend strength and impact-tolerance were separately increased by 3.1%, 51.66% and 60.7%; and heat-resistance obtained by DMA were shown better thermal stability.



*Keywords:* composite patch, multi-walled carbon nano-tubes (MWCNTs), mechanical properties, thermal propertie

## 1. Introduction

Multi-walled carbon nano-tubes of MWCNTs, a new type of quasi-one-dimensional functional material, is increasingly attracting scientific and industrial interest by virtue of their outstanding characteristics, such as good mechanical behavior, electrical properties and thermal properties. Research results on the effect of MWCNTs on the properties of several composite materials have been reported by Kim et al. (2007), Lee et al. (2011), Baker (1999), Barkoula et al. (2009), Chalkley et al. (1999), Chen et al. (2007), Fu (2008), Wang et al. (2004), Chen et al. (2007) and Lee et al. (2010). In this research two kinds of composite patch were prepared, multi-walled carbon nano-tubes and carbon fibre reinforced epoxy resin of MWCNTs/CF/EP and carbon fibre reinforced epoxy resin of CF/EP, and

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doi:10.1016/j.phpro.2013.11.062

theirs mechanical properties and thermal properties were investigated by using universal testing machine and DMA. The immersion and combination between fibre and resin were observed by SEM.

## 2. Experimental

### *2.1. Materials*

The epoxy resin used in the study was the pre-polymers prepared by mixing of the epoxy resin E-51, E-44, Diglycidyl-4,5-epoxycyclohexane-1,2-dicarboxylate and 4,4'-Bi(dichloro-s-triazinyl) aminodiplenylmethane, and 4,4'-diamino diphenyl sulfone(DDS) was used as the curing agent. The coupling agent KH-570 was bought from Lanxingchenguang Chemical Academe. The cloth of carbon fibre, CF-3031, is produced by Toray Industries, with 0.25mm thickness and 220g/m2. Multi-walled carbon nano-tube (MWCNT-1020) was produced by Shenzhen Nanotech Port Co., Ltd. in Shenzhen of China, with 10-20nm diameter, 5-15μm length and a purity of 98%.

### *2.2. Sample*

Pre-polymers of the epoxy resin were heated and mixed with DDS uniformly at 100 ℃ . And then added MWCNTs into the mixture, made them disperse uniformly by the ultrasonic disperse machine. Two kinds of MWCNTs/EP and EP were obtained after sucking at a vacuum for 20min. By the hand lay-up method the two types of resin were smeared into the surface of fibre cloth with coupling agent treated. It had been hold for 1h at 70℃ by the method of hot-melt impregnation, and then cured in an autoclave at 120℃ for 2h by the vacuum bag molding, which was performed using composite hot bonder CMR-1A, after being cut as the GB/T3356-1999, GB/T 1043-93 and JC/T 773-1982 into certain shapes for separately preparing the specimens of bend strength, impact-resistant and interlaminar shear strength.

### *2.3. Methods*

Bending tests were performed using an Instron Model WDW-100 universal testing machine at 4 mm/min rate. Impact test was performed using the impact testing machine AFS/MK3 at 2.9m/s rate. The conditions included impact energy of 4J, and support line space of 60mm. For interlaminar shear test, the specimen was tested by the method of three points bending at 1mm/min rate. Ten specimens were tested to get the average result. The frature surfaces of the composites were obtained from the mechanical test specimens, and examined using scanning electron microscopy (SEM) s4800. For the thermal mechanical properties of the composite patch, it was performed using the dynamic thermal mechanical analyzer (DMA242). Treatment conditions included a frequency of 1Hz, a temperature range from 0℃ to 260℃ applied at a heating rate of 2℃/min.

## 3. Result and discussion

### *3.1. SEM of composite patch's section*

The SEM image of composite patch section was shown in Fig. 1. For each composite patch, the resin was fully soaked into the carbon fibre and thereby the interface of resin and fibre was connected compactly, with no defects of obvious resin enrichment and insufficient gel content. So we can conclude that MWCNTs have a weak influence on the soakage, although make the viscidity of epoxy increase.

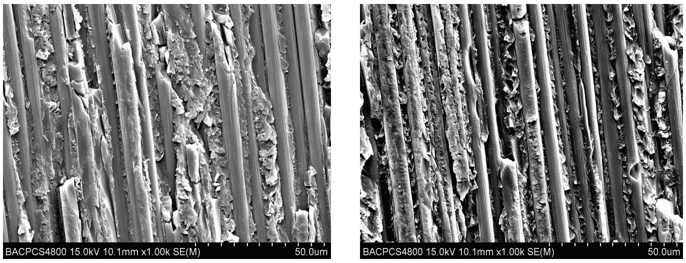


Fig. 1. SEM image of composite patch section (a) CF/EP; (b) MWCNTs/CF/EP

### *3.2. The effect of MWCNTs on the mechanical properties of composite patch*

The interlaminar shear strength of the composite patch could effect directly on its repair strength for the damaged structure. Adding MWCNTs into the epoxy was expected to have a positive influence on the interlaminar shear strength in this research, and the result is shown in the Table 1. This experiment demonstrates that the interlaminar shear strength of MWCNTs/CF/EP composite patch is increased by 3.1%, and bend strength and bend modulus are increased separately by 51.66% and 13.72%, and the impact-tolerance is increased by 60.7%, compared to the CF/EP composite patch.

Table 1. The mechanical properties of composite patch

| Composite patch | Interlaminar shear strength (*MPa*) | Bend strength ( *MPa*) | Bend modulus (*MPa*) | Impact-tolerance strength ($kJ/m^2$) |
|---|---|---|---|---|
| CF/EP | 40.18 | 512.89 | 48.21 | 59.42 |
| MWCNTs/CF/EP | 41.42 | 777.88 | 54.83 | 95.50 |

The fractography of composite patch was performed using SEM as shown in Fig. 2 after testing intelaminar shear strength. For the MWCNTs/CF/EP composite patch, the wholes' shape of little cracks seen in Fig. 2(b) is presented shorter and narrower. Thus, the addition of MWCNTs can obviously improve the interlaminar shear property of the composite patch, may due to a good interfacial performance between fibre and resin with the function of the MWCNTs.

The fractography of composite patch after testing impact-tolerance was observed by SEM as shown in Fig. 3. In Fig. 3(a), the phenomenons of fibre fallout, debonding and the gel content insufficient on the fallout fibre are apparent, so the interface combination between resin and fibre of CF/EP composite patch is worse than that of MWCNTs/CF/EP composite patch as shown in Fig. 3(b).

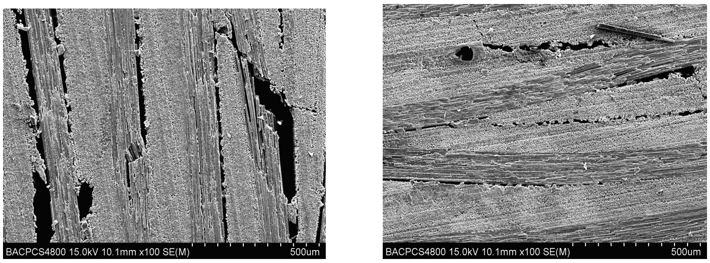


Fig. 2. The fractography of composite patch after testing interlaminar shear strength (a) CF/EP; (b) MWCNTs/CF/EP

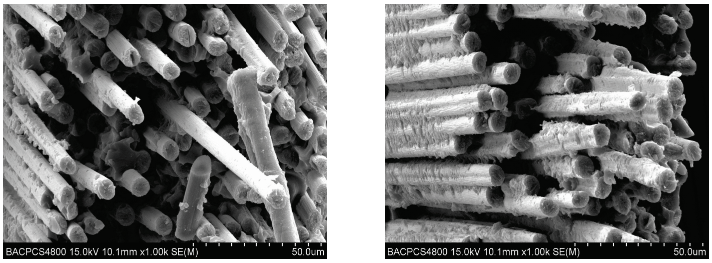


Fig. 3. The fractography of composite patch after testing impact tolerance (a) CF/EP; (b) MWCNTs/CF/EP.

In general, the results indicate that interlaminar shear strength, bend strength and impact-resistant are separately increased by 3.1%, 51.66% and 60.7% for the composite patch with the addition of MWCNTs. The improvement of its mechanical properties is attributed to the improvement of interfacial combination between carbon fibre and epoxy resin caused by the addition of MWCNTs, which has a stronger binding force by the function of specific surface area, and an ability of transferring load effectively in order to achieve the purpose of preventing the crack spreading.

### *3.3. DMA*

The DMA experiments were made to the CF/EP and MWCNTs/CF/EP composite patches, and the curves of storage-modulus ($E'$) versus temperature are shown as Fig. 4(a). The curves show that MWCNTs can make the initial storage-modulus increased, and higher than the composite patch without MWCNTs in the range of the test temperature. It is noted that MWCNTs can increase the crosslink-density of the composite patch and its stiffness.

The curves of loss-modulus ($E''$) versus temperature are shown in Fig. 4(b). With the temperature increasing, the loss-modulus is presented the same rising trend at the beginning, whereas the different maximum of $E''$. After adding MWCNTs, the viscosity of the composite was increased and consequently the motions of epoxy molecules needed more energy to conquer the inner friction, so what directly lead to increase the loss-modulus and move to high temperature for the location of maximum.

Fig. 4(c) shows the curves of tan$\delta$ versus temperature for the CF/EP and MWCNTs/CF/EP composite patch, respectively. For the MWCNTs/CF/EP composite, there are two significant peak of 86.62℃and 159.04℃, compared to 89.29℃of the CF/EP composite. And the height of the first peak is lower than the composite without MWCNTs, but the second peak is even higher. In this study, the difference of $T_g$ and tan$\delta$ of the first peak may be attributed to the difference in the extent of cross-linking reactions of epoxy in the initial reactions, and a higher cross-linking network at the higher temperature than do the CF/EP composite. Furthermore, due to the MWCNTs functionality, a strong interfacial bond and good dispersibility reduce the mobility of epoxy molecules around the MWCNTs, and so result in increased thermal stability[10].

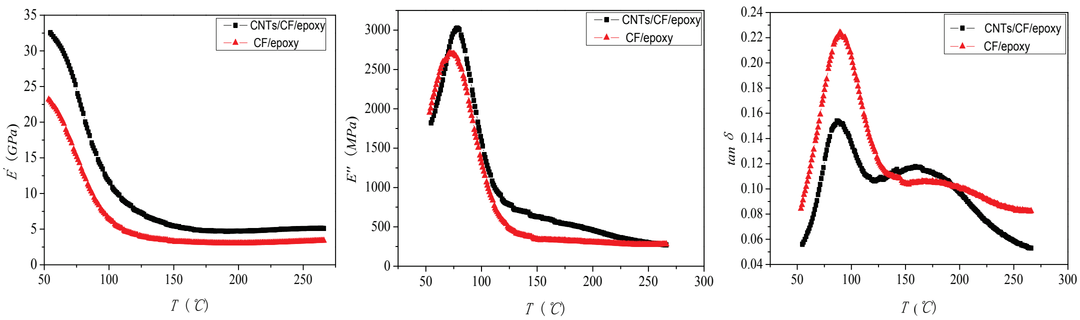


Fig. 4. The DMA of two kinds of composite patch (a) storage-modulus ($E'$); (b) loss-modulus ($E''$) ; (c) loss-factor(tan$\delta$)

In the same case of the ply angle of carbon fibre and curing process, MWCNTs has an important effect on the curing reaction of the composite patch, including the improvement of the crosslink density, the inner friction of molecular movement and thermal stability.

## 4. Conclusion

The results indicate that the addition of MWCNTs can make the mechanical properties of composite patch including interlaminar shear, bend and impact-tolerance increased by 3.1%, 51.66% and 60.7%, individually. The analysis of SEM shows that the interface between carbon fibre and resin combines well for the composite patch, whether reinforced or unreinforced with MWCNTs, and carbon fibre is fully soaked into the resin. The analysis of composite patch by DMA indicates that MWCNTs can improve its thermal stability, with the crosslink density of epoxy resin and inner friction of molecular movement increased.

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